# PHOTOCATALYTIC ACTIVITY AND KINETIC STUDY OF DYE REMOVAL OVER $CuFe_2O_4$ UNDER VISIBLE LIGHT IRRADIATION

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Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
Bachelor of Chemical Engineering

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JANUARY 2014

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# ABSTRACT

The contamination of water resources by industrial effluents containing toxic dyes have serious problem to the human society and environment. The high concentration and higher stability of modern synthetic dyes makes conventional method ineffective for complete degradation of dyes. An advanced oxidation processes (AOPs) is a new technology for treating wastewater based on the generation of hydroxyl radicals (·OH) by using semiconductor assisted photocatalytic degradation. Organic contaminants attacked repeatedly by ·OH leads to complete oxidation. Therefore, this work aims to synthesize and characterize copper ferrite, $CuFe_2O_4$ photocatalyst which is active under visible light irradiation for dye removal. $CuFe_2O_4$ have been prepared by co-precipitation method and undergoes calcination at $300^oC$ for 2 hours. Physicochemical characterization revealed that the catalyst has BET specific surface area of 13.23 $m^2/g$ and band gap energy of 1.71 eV. The presence of $CuFe_2O_4$ was confirmed via XRD pattern at 2θ of $30.37^o$, $36.00^o$, $42.75^o$ and $62.62^o$ respectively. Moreover, crystalline size was in the range of 8.5 to 12.9 nm. The adsorption equilibrium of $CuFe_2O_4$ system was found to follow Langmuir adsorption model with adsorption equilibrium constant of $1 \times 10^{-2}$ L/mg and maximum adsorption capacity of 8.38 mg/g. The effects of catalyst loading and initial concentration of dye were investigated. The photo-degradation of methylene blue (MB) increased with catalyst loading owing to more $CuFe_2O_4$ active sites. In contrast, the dye degradation decreased when the initial concentration was increased. This can be explained by the attainment of maximum efficiency by $CuFe_2O_4$ photocatalyst. In addition, the Langmuir-Hinshelwood (L-H) models were employed to capture the kinetic trend. Results from the modelling exercise showed that photo-degradation adhered to L-H models and that the reaction constant was 0.131 mg/L.min. The high degradation of MB suggests that $CuFe_2O_4$ has promising potential in treating actual dyes-containing wastewater.

# ABSTRAK

Pencemaran sumber air oleh efluen industri yang mengandungi pewarna toksik memberi kesan yang serius kepada manusia dan alam sekitar. Kepekatan yang tinggi dan kestabilan pewarna sintetik moden yang lebih tinggi menjadikan kaedah konvensional tidak berkesan untuk merawat efluen yang tercemar sepenuhnya. Kaedah proses pengoksidaan lanjutan (AOPs) adalah teknologi baru untuk merawat air sisa berdasarkan generasi radikal hidroksil (·OH) dengan menggunakan degradasi fotokalatilik yang dibantu semikonduktor. Bahan cemar organik yang diserang berulang kali oleh ·OH membawa kepada pengoksidaan yang lengkap. Oleh itu, kerja ini bertujuan untuk mensintesis dan mencirikan ferit tembaga, $CuFe_2O_4$ fotokatalis yang aktif di bawah penyinaran cahaya tampak untuk penyingkiran pewarna. $CuFe_2O_4$ telah disediakan dengan kaedah pemendakan bersama dan menjalani proses kalsinasi pada 300$^oC$ untuk 2 jam. Pencirian fizikokimia mendedahkan bahawa pemangkin mempunyai kawasan permukaan sebanyak 13.23 $m^2/g$ dan jurang jalur tenaga sebanyak 1.71 eV. Kewujudan $CuFe_2O_4$ telah disahkan melalui corak XRD di 2θ pada 30.37$^o$, 36.00$^o$, 42.75$^o$ dan 62.62$^o$. Selain itu, saiz kristal adalah dalam julat 8.5 – 12.9 nm. Adalah didapati bahawa keseimbangan penjerapan sistem $CuFe_2O_4$ mengikuti model penjerapan Langmuir dengan pemalar keseimbangan penjerapan 1 x $10^{-2}$ L/mg dan kapasiti penjerapan maksimum sebanyak 8.38 mg/g. Kesan muatan pemangkin dan kepekatan awal pewarna telah disiasat. Degradasi metilen biru (MB) meningkat dengan muatan pemangkin kerana lebih banyak tapak aktif pada permukaan $CuFe2O_4$. Sebaliknya, degradasi pewarna menurun apabila kepekatan awal semakin meningkat. Ini dapat dijelaskan oleh pencapaian kecekapan maksimum $CuFe_2O_4$. Di samping itu, model Langmuir-Hinshelwood (L-H) digunakan untuk menentukan trend kinetik. Keputusan dari pemodelan menunjukkan bahawa degradasi fotokatalitik mematuhi model L-H dan malar tindak balas adalah 0.131 mg/L.min. Degradasi MB yang tinggi menunjukkan bahawa $CuFe_2O_4$ mempunyai potensi yang tinggi untuk merawat air sisa sebenar yang mengandungi pewarna.

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# LIST OF ABBREVIATIONS

| | |
|---|---|
| E | band gap of semiconductor in equation (2.1) |
| r | rate of degradation or oxidation in equation 2.23) |
| $K_r$ | Langmuir-Hinshelwood rate constant in equation (2.23) |
| k | Langmuir adsorption constant in equation (2.23) |
| C | Concentration of MB in equation (2.23) |
| q | amount of dye adsorbed per gram of adsorbent at equilibrium for equation (3.1) |
| $q_\alpha$ | maximum adsorption capacity in equation (3.1) |
| K | adsorption equilibrium constant for equation (3.1) |
| $C_e$ | equilibrium dye concentration in equation (3.2) |
| $C_o$ | initial dye concentration for equation (3.2) |
| v | volume of methylene blue in equation (3.3) |
| w | weight of photocatalyst in equation (3.3) |
| $R^2$ | coefficient of determination |
| $k_{app}$ | apparent first-order rate constant |

Greek

| | |
|---|---|
| $\lambda$ | *wavelength of photon in nm* |
| $\theta$ | *angle in degree* |

# LIST OF ABBREVIATIONS

| | |
|---|---|
| AOP | Advanced oxidation process |
| XRD | X-ray Diffraction |
| VOC | Volatile organic compound |
| EHP | Electron-hole pair |
| UV | Ultraviolet |
| IR | Infrared |
| CFC | Chlorofluorocarbon |
| MRI | Magnetic resonance imaging |
| JCPDS | Joint Committee on Powder Diffraction Standards |
| hv | light energy |
| MB | methylene blue |
| L-H | Langmuir-Hinshelwood |
| DRS | diffuse reflectance spectrum |
| ARB | Acid Red B |

# CHAPTER 1

# INTRODUCTION

## 1.1 Background

Wastewater treatment takes effluent from water users (private homes, business or industrial sources) as influent to wastewater treatment facilities. The wastestream is treated in a series of steps of processes and then discharged to a receiving body which is usually a river or stream (Drinan, 2001). Wastewater treatment takes the wastes and water that comprise the "wastestream" and restores the wastewater to its original quality. The main goal of wastewater treatment is to treat the wastestream to the level that it is harmless to the receiving body (Drinan, 2001).

Generally there are 3 characteristics of wastewater. The 3 types of characteristics are physical, chemical and biological characteristics (Drinan, 2001). Wastewater parameters provide a yardstick by which to assess the physical, chemical and biological characteristics of wastewater. Meeting these parameters before discharge ensures the wastewater released into surface water presents no chance of harm or disruption to the environment or to humans within a wide range of possible water uses (Drinan, 2001).

The existence of biological wastewater characteristics is due to the fact that the presence or absence of pathogens in wastewater is of primary importance. Normal sewage contains millions of harmless microbes per milliliter (mL). However, wastes from people infected with disease can produce harmful pathogenic organisms that then enter the sewage and the water systems receiving the sewage. While the processes that treat wastewater involve using the life-cycles of many types of bacteria and protozoa for removing the wastes from the water, the final effluent to be released must not carry dangerous levels of pathogens into the receiving waters (Drinan, 2001).

The wastewater physical characteristics of concern include the presence and quantity of solids in the wastestream, the degree of turbidity, the colour of wastewater, temperature and odour of wastewater (Drinan, 2001). On the other hand, the major chemical parameters of concern in wastewater treatment are total dissolved solids, alkalinity, metals organics and nutrients, pH and chlorides. These chemical parameters are directly related to the solvent capabilities of water (Drinan, 2001). Lastly, the major biological characteristics of concern in wastewater treatment include the presence of bacteria, viruses, algae, protozoa and parasitic worms (Drinan, 2001).

Wastewater is the flow of used water from a community, and includes household wastes, commercial and industrial wastestream flows, stormwater, and groundwater. According to Drinan (2001), wastewater comprise of 0.6% solids (suspended or dissolved materials) carried in the 99.4% water flow. This extreme ratio of water to solids is essential to transport solids through the collection system. The solids found in wastewater rarely contain only what most people consider sewage (human wastes). In fact, the dissolved and suspended solids in sewage can varies widely from community to community, and is dependent on what inflow industrial and commercial facilities contribute to the treatment collection system.

A different type of sources of wastewater contains different constituents. Common industry practice puts these constituents into several categories, human and animal wastes, household wastes, industrial wastes, stormwater runoff and groundwater infiltration (Drinan, 2001). Human and animal wastes are generally thought as the most dangerous wastewater constituent from a human health viewpoint. Domestic wastewater contains solid and liquid discharges of humans and animals. These contribute millions of bacteria, virus and other organisms (some pathogenic) to the wastewater flow (Drinan, 2001).

On the other hand, household wastes such as domestic or residential wastewater flow may also contain paper, household cleaners, detergents, trash, garbage and any other substance that a typical homeowner may pour or flush into the sewer system. In collection systems that carry both community wastes and stormwater runoff, during and after storms wastewater may contain large amounts of sand, gravel, road-salt, and other grit, as well as flood-levels of water. Many communities install separate collection systems for stormwater runoff, in which the influent should contain grit and street debris, but no domestic or sanitary wastes. Groundwater infiltration is due to old and improperly sealed collection systems that permit groundwater to enter the system through cracks, breaks or unsealed joints. This can add large amounts of water to the wastewater flow, as well as additional grit (Drinan, 2001).

Above all, industrial wastes have the most possible types of materials to be discharged from industrial processes into a collection system. These materials include chemicals, dyes, acids, alkalis, grit, detergents and highly toxic materials. Individual industries present highly individual wastestreams, and these industry-specific characteristics depend on the industrial process used. While many times industrial wastewaters can be treated within public treatment facilities without incident, often industries must provide some level of treatment prior to their wastestream entering a public treatment. This is necessary to avoid compliance problems for the treatment facility. Drinan (2001) also states that an industry may also choose to provide pretreatment because their own on-site treatment is more economical than paying municipality fees for advance treatment.

Wastewater treatment currently uses technology such as adsorption process. Adsorption is efficient but once toxic compounds adsorbs on the adsorbents, they became hazardous wastes that need to be disposed or treated properly (Wu et al., 2004). One new technology for treating wastewaters is the advanced oxidation processes (AOPs) (Mesgari et al., 2012). AOPs are based on the generation of hydroxyl radicals (·OH) that degrades a broad range of organic pollutants. In many cases, dyes are studied as model compounds for large organic molecules (Casbeer et al., 2012). In that case, photocatalyst are able to generate ·OH which are then able to degrade organic contaminants.

The word photocatalysis is a composite word which is composed of two parts, “photo” and “catalysis” (GENS, 2013). Catalysis is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered or consumed at the end. This substance is known as the catalyst which increases the rate of reaction by reducing the activation energy. Photocatalysis is a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without being involved itself (GENS, 2013). Photocatalyst is the substance which can modify the rate of chemical reaction using light irradiation.

Chlorophyll of plants is a typical natural photocatalyst. The difference between chlorophyll photocatalyst to man-made photocatalyst is, usually chlorophyll captures sunlight to turn water and carbon dioxide into oxygen and glucose, but on the contrary photocatalyst creates strong oxidation agent and electronic holes to breakdown organic matter to carbon dioxide and water in the presence of photocatalyst, light and water (APRA, n.d.).

## 1.2 Motivation (current issue and potential solution)

The contamination of water resources by industrial, agricultural and domestic effluents is posing a great problem to the human society. Today, various water and wastewater treatment processes has been developed and employed. According to Wu et al. (2004), the safest methods to the environment for wastewater treatment is by complete mineralization of organic pollutants. Various methods of treating wastewater such as biotechnology, chemical oxidations and adsorption have been studied for the treatment of organic pollutants in water (Lee et al., 2001; Bertanza et al., 2001). However, some contaminants such as aromatic halide or nitro aromatic substances and dyes have adequate resistance to oxidation by bio-degradation and conventional chemical oxidation (Wu et al., 2004). Therefore, the removal of organic pollutants remains a great challenge (Tolosa et al., 2011).

Much attention is given to the decolourization of dyes in the industrial wastewater (Mesgari et al., 2012). It was reported that about 1-20% of the total world production of dyes is lost during the dyeing process and are released into the environment as textile effluent (Zollinger, 1991). Organic dyes produce toxic substances through oxidation, hydrolysis or other chemical reaction occurring in wastewater phase (Neppolian et al., 2002). The high concentration of organics in the effluents and the higher stability of modern synthetic dyes make conventional method ineffective for complete removal and degradation of organic dyes (Hamza & Hamoda, 1980; Gandhi et al., 2008). Hence, wastewaters containing toxic organic dyes have serious problems to the environment (Akpan & Hameed, 2009). Other conventional methods of colour removal from an aqueous medium include technique like coagulation, filtration, treatment with ozone and adsorption (Lorimer et al., 2001).

In view of growing concern of environmental issue, alternative techniques must be found to solve the problem. Adsorption process and catalytic oxidation technologies are promising methods for removal of various contaminants and have been studied for the removal of organic refractory pollutions from water (Lee et al., 2001).

Adsorption process is one of the effective methods with the advantage of high treatment efficiency and no harmful by-product to treated water (Allen, 1996). However, adsorption process only transfers pollutants from one phase to another rather than eliminating them from the environment. Thus, they became hazardous wastes that needed to be treated or disposed properly (Wu et al., 2004). It is also common where currently used technologies for removing contaminants require the compounds to be transferred between phases or from the source to treatment facilities. The transfer can be effective in removing contaminants from the environment, but additional treatment or disposal of waste products are required for complete removal (Casbeer et al., 2012).

According to Kostedt et al. (2005), repeated attacked of organic contaminants by ·OH leads to complete oxidation. AOPs are of ample interest currently for the effective oxidation of a wide variety of organics and dyes (Boye et al., 2002). Among them, top priority goes to semiconductor assisted photocatalytic degradation. Most of the photocatalytic studies use either synthetic or commercial titanium dioxide ($TiO_2$) as photocatalyst (Grzechulska & Morawski, 2002). $TiO_2$ dominated the field of catalysis due to several properties such as its moderate band gap (3.2 eV), low cost, high surface area, non-toxic, recyclability, high photoactivity, wide range of processing procedures and its excellent chemical and photochemical stability (Wade, 2005).

The band gap of $TiO_2$ requires light with wavelength equal or shorter than 385 nm (UV-A) or higher energy photon. This is highly inefficient for the use with visible light, as there is only 5% of sunlight emitted at wavelength below 385 nm (Wade, 2005). Because of this, $TiO_2$ is unable to utilize sunlight efficiently. For this reason, many scientists are looking to new photocatalytic system for the solution. One approach is to develop photocatalyst which can utilize the available solar spectrum and not limited on the UV spectrum. Visible light photocatalysis is currently being pursued across the globe, including research groups from countries such as Japan, China, France, South Korea, United States of America, United Kingdom, Germany, Canada, Italy and Taiwan (Wade, 2005). Even though the current success of these photocatalysts has been limited, the immediate and long term applications are required to solve the problems of environmental pollution. This is because environmental pollution is proposed to be the greatest problem that chemical scientist will face in the 21$^{st}$ century (Wade, 2005).

Currently, typical visible light photocatalyst such as cadmium sulphide (CdS) and iron (III) oxide has disadvantages such as little or no photoactivity or experience photocorrossion (De et al., 1996; Hwang et al., 2002). On the other hand, novel visible light photocatalyst such as $Bi_2Fe_4O_9$ and $CaBi_2O_4$ which were prepared using solid state reaction have small specific surface areas which is liable to lower photocatalytic activities (Chen et al., 2010). Therefore developing efficient methods to fabricate novel visible-light photocatalyst with excellent photocatalytic activity is urgently needed. The particle size of fabricated photocatalyst must be very small so that it has high surface area which increases its photocatalytic activity and the band gap of the photocatalyst must be narrow so that it can utilize solar energy effectively (Casbeer et al., 2012).

Since doping $TiO_2$ with heavy metals such as platinum and gold expensive, one way is to develop new material to replace $TiO_2$. A new generation of photocatalyst must be created to utilize the available solar spectrum effectively (Wade, 2005). For this purpose, spinel ferrites have high potential as majority of the ferrites have narrow band gap (≤ 2.2 eV) (Casbeer et al., 2012). Copper ferrite ($CuFe_2O_4$) has an exceptionally low band gap, 1.32 eV (Derbal et al., 2008) and this makes it promising candidate for visible light active photocatalyst. The spinel crystal structure enhanced the efficiency due to the available extra catalytic sites by virtue of the crystal lattice (Dom et al., 2011). According to Casbeer et al. (2012), the use of ferrites for the degradation of contaminants in water has gained much interest recently. Both organic and inorganic contaminants such as specific dyes and bacteria have been studied. As other types of ferrites such as zinc ferrite (1.92 eV) shows some promising results (Casbeer et al., 2012). There is no doubt that $CuFe_2O_4$ which has not been tested as photocatalyst for dye removal or wastewater treatment offers a great potential. With much lower band gap, 1.32 eV, $CuFe_2O_4$ has a great potential as a photocatalyst for environmental purification particularly in wastewater treatment is promising.

## 1.3 Problem statement

Pollutants such as dyes have adequate resistance to oxidation by bio-degradation and conventional chemical oxidation. Hence wastewaters containing toxic dyes have serious problems to the environment. Therefore, the need to synthesize photocatalyst which is active under visible light irradiation is crucial so that it can utilize solar energy efficiently while treating wastewater containing organic contaminants such as dyes effectively.

## 1.4 Objectives

This work aims to synthesize, characterize and perform kinetic study on photocatalyst that is active under visible light irradiation for dye removal.

## 1.5 Scope of this research

In order to meet the outlined objective, the following scopes of research have been identified. $CuFe_2O_4$ photocatalyst will be synthesized using co-precipitation method adapted from Wu et al. (2004). The synthesized $CuFe_2O_4$ will be characterized using several techniques.

$CuFe_2O_4$ photocatalyst will be characterized using the following techniques:

1) BET Surface Analyser
2) X-ray Diffraction (XRD)
3) UV-vis diffuse reflectance spectrum (DRS)

The photocatalytic activity of $CuFe_2O_4$ will be evaluated using methylene blue (MB) dye as a model compound for organic contaminants. The photocatalytic activity of $CuFe_2O_4$ can be evaluated by the percentage of degradation of MB before and after treatment with $CuFe_2O_4$ photocatalyst. The results obtained will be discussed and compared with previous study reported by Casbeer et al. (2012) on photocatalytic degradation of MB by ferrite. A series of experiments will be conducted to study the effect of catalyst loading and effect of initial concentration of MB dye. The kinetic data obtained from experimental work will then be evaluated using suitable model. An experiment on the adsorption of MB on $CuFe_2O_4$ will also be carried out.

## 1.6 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides a review on the literature on the topic of photocatalysis in eleven sections. The first section introduces the important topics in this chapter. In the second section, the history of photocatalysis was reviewed. In the third section, the band gap theory was explained. The development of visible light photocatalyst was discussed in the fourth section. Fifth section is where photocatalytic oxidation is explained. In the sixth section, current and future applications of photocatalyst were discussed. The seventh section was where the mechanism of photocatalysis was explained. In the eight section, the potential of copper ferrite as photocatalyst was accessed. The ninth section is where synthesis of ferrites was examined. The tenth section is where common organic dyes were inspected. Lastly, the eleventh section is where kinetic study was explored.

Chapter 3 describes the materials and experimental procedures for this study. Details on the materials and chemicals required, step-by-step procedures to synthesize and testing the photocatalyst were presented.

Chapter 4 presented the results from photocatalyst characterization and laboratory work. The first section represents the outline of results and discussion. In the second section, characterization of photocatalyst was discussed. The third section is where the results of adsorption of MB on $CuFe_2O_4$ were evaluated. The fourth section is where photocatalytic activity of $CuFe_2O_4$ was accessed. In the fifth section, kinetic analysis of photocatalytic degradation of $CuFe_2O_4$ was performed. Lastly, the sixth section is where comparison with previous work was carried out.

Chapter 5 draws together a summary of the thesis and outlines the future work and improvement which can be carried out based on current work.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Overview

There are eleven sections in this chapter, which are introduction, history of photocatalysis, band gap theory, development of visible light photocatalyst, photocatalytic oxidation, application of photocatalyst, mechanism of photocatalysis, copper ferrite as potential photocatalyst, synthesis of ferrites, organic dyes and kinetic study.

## 2.2 Introduction

This paper presents an in-depth study on photocatalysis. Important information of photocatalysis such as the synthesis methods, mechanism of photocatalysis and development of photocatalyst were presented.

## 2.3 History of photocatalysis

Catalysis is an umbrella term to describe any process in which a substance through intimate reaction(s) with reactant(s) through a lower activation energy (Wade, 2005). Many processes can be found under catalysis, such as photocatalysis, thermal catalysis, redox catalysis and enzyme catalysis. Photocatalysis has become an increasingly important field and a heavily researched topic by all fields of science, including chemists and physicist. Today, photocatalysis is pursued to solve an ever-widening variety of environmental problems.

According to Wade (2005), the term photocatalysis has been used since 1920s. Photocatalysis broadly defines a photoreaction that is accelerated by the presence of catalyst. In the mid-1920s, semiconductor zinc oxide (ZnO) began attracting attention for use as sensitizer for the decomposition of both organic and inorganic photoreactions, and $TiO_2$ was soon investigated for its photodegradation characteristics (Mills & Le-Hunte, 1997).

Most of the primitive work on photocatalyst started in 1960s, leading to the first photochemical cell for splitting water using n-type $TiO_2$ and platinum (Pt) coated electrodes in 1969 (Fujishima & Honda, 1972). This photoelectrochemical decomposition of water happens under irradiation of light without any applied electric power. The $TiO_2$ electrode was illuminated under short circuit condition, $H_2$ evolved at the Pt electrode and oxygen evolved at the $TiO_2$ electrode.

This great discovery has attracted worldwide attention and sparked enormous research in the effort to find semiconductors that are able to utilize the available solar spectrum effectively. In early 1980s, $TiO_2$ was used for the first time to sensitize reactions in the photomineralization of selected organics. The field of photocatalysis has been dominated by studies on photocatalytic oxidation of organic compounds in water and there are increased interest in oxidizing bacteria and volatile organic chemicals (VOCs) for the purpose of air purification (Wade, 2005).

Over the years, many semiconductors with photocatalytic properties have been investigated or partially investigated, including $TiO_2$ (3.2 eV), strontium titanate ($SrTiO_3$) (3.4 eV), iron (III) oxide ($Fe_2O_3$) (2.2 eV), cadmium sulphide (CdS) (2.5 eV), tungsten trioxide ($WO_3$) (2.8 eV), zinc sulphide (ZnS) (3.6 eV), iron titanium oxide ($FeTiO_3$) (2.8 eV), zirconium dioxide ($ZrO_2$) (5 eV), vanadium (V) oxide ($V_2O_5$) (2.8 eV), niobium pentoxide ($Nb_2O_5$) (3.4 eV), tin dioxide ($SnO_2$) (3.5 eV) and many others (Xu & Schoonen, 2000; Blake, 1999).

By far $TiO_2$ has been dominated the field of catalysis in terms of research, characterization and applications (Wade, 2005). $TiO_2$ attracted much research is due to its moderate band gap, non-toxicity, high surface area, low cost, recyclability, high photoactivity, wide range of processing procedures and its excellent chemical and photochemical stability (Wade, 2005). $TiO_2$ is also ranked as one of the top 50 most available chemicals, ensuring it will be around at low cost for some time (Wade, 2005; Wikipedia, 2013).

However $TiO_2$ band gap of 3.2 eV requires a photon with wavelength equal or shorter than 385 nm to excite this semiconductor, meaning that it needs to be a UV-A or higher energy photon. This band gap is favourable for UV photocatalysis, but subjects to low efficiency yields in solar applications (largest potential market) since less than 5% of the sun's energy is emitted at wavelength below 385 nm. Therefore, the most active form of $TiO_2$, anatase form is considered an ideal photocatalyst for UV applications (Wade, 2005). Unmodified form of anatase $TiO_2$ rendered highly inefficient for visible light application.

## 2.4 Band gap theory

When a semiconductor or photocatalyst is irradiated with photons with energies greater than that of the semiconductor's band gap, an electron (e-) is transferred to the conduction band, leaving behind a positive hole ($h^+$) in the valence band. The pair of photoexcited charges that occurs within the particle is called electron-hole pair (EHP). The produced e- and $h^+$ enable oxidation and reduction processes to occur. The energy required by a photon to generate EHP in a photocatalyst can be related to its wavelength (Wade, 2005) in the following equation:

$$\lambda(\text{nm}) \leq \frac{1240}{\text{E}} \qquad (2.1)$$

where,

$\lambda$ = wavelength of photon in nm

E = band gap of semiconductor in eV

Using equation 2.1,

Wavelength required by $TiO_2$ (3.2 eV) = $\frac{1240}{3.2}$ = 387.5 nm or less

Wavelength required by $CuFe_2O_4$ (1.32 eV) = $\frac{1240}{1.32}$ = 939.4 nm or less

Generally, visible light is categorized with photon of wavelength from 390 nm to 780 nm. Visible light of different colours have different wavelength (ICRA, 2012). The wavelength of visible light is shown in Table 2-1. Solar energy that reaches Earth's surface is made of ultraviolet (UV), visible and infrared (IR) irradiation. According to Sen (2008), sunlight that reaches Earth's surface is of 46% visible, 5% UV, and 49% IR irradiation. The solar energy spectrum is shown in Figure 2-1.

Using equation 2.1,

The maximum band gap to be visible light active = $\frac{1240}{390}$ = 3.179 eV

Band gap required to stay active in visible light of any colour = $\frac{1240}{780}$ = 1.59 eV

Table 2-1: Wavelength of visible light (ICRA, 2012).

| Colour | Approximate wavelength, λ (nm) |
|---|---|
| White | 390-780 |
| Violet | 390-455 |
| Blue | 455-495 |
| Green | 495-575 |
| Yellow | 575-600 |
| Orange | 600-625 |
| Red | 625-780 |

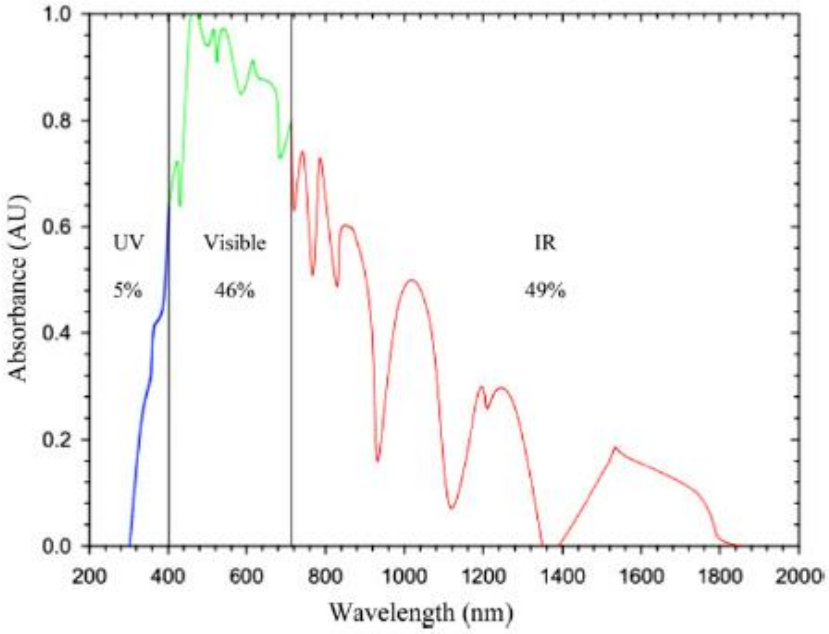


Figure 2-1: Solar energy spectrum (Sen, 2008).

From Table 2-1, it is clearly seen that $TiO_2$ with a band gap of 3.2 eV will not be able to generate any EHP in visible light since the minimum wavelength required, 387.5 nm is shorter than the wavelength of visible light of any colour. On the other hand, $CuFe_2O_4$ is able to generate EHP in visible light of any colours theoretically since the minimum wavelength of 939.4 nm can be satisfied easily using visible light of any colour.

## 2.5 Development of visible light photocatalyst

Much of the focus on photocatalyst to date has been on $TiO_2$ (Sharma & Chenay, 2005). However, $TiO_2$ has a wide band gap of 3.2 eV and therefore can absorb only a small portion of sunlight. It is ideal to use visible solar energy due to the large amount that reaches the Earth's surface annually, which is approximately 10,000 times more than the current yearly energy consumption (Gratzel, 2001). Therefore, developing photocatalyst capable of utilizing safe and sustainable solar energy effectively and efficiently is important.

There are two approaches in which visible light irradiation can be utilized by photocatalyst (Tang et al., 2004). One approach is by doping a UV-active photocatalyst with elements in an effort to make them visible light active (Martyanov et al., 2004; Yang et al., 2005; Anpo & Takeuchi, 2003). Doped semiconductors are known to behave as efficient photocatalyst due to possible effects on the band energies and the consequent electron-hole charge separation (Borse et al., 2011). Doping semiconductors results in an increased density of states in the band structure that yields high photocatalytic activity. The use of dopants into $TiO_2$ narrows the band gap so that $TiO_2$ effectively absorbs visible light. The introduction of transition metal ion results in formation of a doping energy level between conduction and valence band of $TiO_2$ and shifts the band gap into the visible region. A dopant may also acts as a trap for electrons or holes and increases photoactivity of doped $TiO_2$ under visible irradiation (Mesgari et al, 2012).

Common dopants that have been used include nitrogen (Fu et al., 2006), carbon (Irie et al., 2003), sulphur (Gorska et al, 2009), combinations of nitrogen, carbon and sulphur (Gorska et al., 2009; Zhou & Yu, 2008), silicon (Wu et al., 2006) or zeolites (Bossmann et al., 2009). Even heavy metals have also been used to dope $TiO_2$ in the effort to make them visible light active (Casbeer et al., 2012). Examples include cobalt (Hsieh et al., 2009), silver (Zielinska et al., 2010), gold (Luo et al., 2011), platinum (Li et al., 2008) and ruthenium (Senthilnanthan et al., 2010).

Even so, the photoactivity of doped $TiO_2$ depends heavily on the preparation method, nature of the dopant ion and concentration and also thermal treatment (Dvoranova et al., 2002). Doping $TiO_2$ with metals such as Cr, Fe, Zr or Mo is detrimental to the photocatalytic activity of $TiO_2$ as a result of the high electron density about the nucleus (Akpan & Hameed, 2010).